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Final report on AOARD 08-4014 grant:

DNA-BASED CHIRAL COMPOSITES WITH ENHANCEMENT OF CHIROOPTIC AND NLO EFFECTS FOR NIM APPLICATIONS

Principal Investigators:

Anna Samoc, PhD, Msc

Marek Samoc, PhD, Dsc

Email addresses: anna.samoc@anu.edu.au, marek.samoc@anu.edu.au

Institution: Laser Physics Centre, Research School of Physical Sciences and Engineering,
The Australian National University
Mailing address: Canberra, ACT 0200, Australia
Tel: +61-2-61254611
Fax: +61-2-61250029

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Collaboration

Dr. J.G. Grote, Materials and Manufacturing Directorate, Air Force Research Laboratory,
WPAFB, OH 45433-7702, USA
Prof. P.N. Prasad, Institute for Lasers, Photonics and Biophotonics, SUNY at Buffalo,
NY 14214, USA

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14. ABSTRACT
In March 2008 we started a new research program on enhancement of chirooptic and nonlinear optical properties in composites based on deoxyribonucleic acid (DNA) derived from marine sources (salmon roe). During the first half-year period of the project we worked on preparation and characterization of the hybrid composites that utilize DNA as a chiral template for assembling non-chiral organic conjugated molecules and noble metal nanoparticles. This combination could potentially lead to a system with a negative index of refraction at visible frequencies. The aim is to realize useful negative index materials (NIM) where the negative index is the result of negative bulk permittivity  and permeability  in the UV-VIS-IR range. We expect that - Negative index can occur in the spectral range of strong electronic absorption resonances due to dopants where abnormal dispersion occurs - negative effective index can be found in an optically active (chiral) medium using a chiral route, in which one of the circularly polarized modes is forced to propagate with a negative value of the effective index Our objective was to achieve a new optical material with enhanced chirality and optical nonlinearities through combining helical arrangement of nucleotides in DNA double helix with high polarizability of chromophores such as organic dyes and the -electron conjugated polymer chains.

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Area of Expertise: ADVANCED MATERIALS

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During the first half-year period of the project we worked on preparation and characterization of the hybrid composites that utilize DNA as a chiral template for assembling non-chiral organic conjugated molecules and noble metal nanoparticles. This combination could potentially lead to a system with a negative index of refraction at visible frequencies.
The aim is to realize useful negative index materials (NIM) where the negative index is the result of negative bulk permittivity ε and permeability μ in the UV-VIS-IR range.
We expect that

- Negative index can occur in the spectral range of strong electronic absorption resonances due to dopants where abnormal dispersion occurs
- negative effective index can be found in an optically active (chiral) medium using a chiral route, in which one of the circularly polarized modes is forced to propagate with a negative value of the effective index

Our objective was to achieve a new optical material with enhanced chirality and optical nonlinearities through combining helical arrangement of nucleotides in DNA double helix with high polarizability of chromophores such as organic dyes and the π-electron conjugated polymer chains. *This final report was submitted in compliance with the terms of the grant, though more data analysis is being performed and will be submitted at a later date.*

<u>Workplan</u>

- Work on hybrid composites, which utilize deoxyribonucleic acid as a chiral scaffold for assembling optical chromophores and noble metal nanoparticles.

- Testing DNA intercalators in order to select the most suitable ones for enhancing chirality and nonlinearity of DNA in the visible wavelength range.

<u>Milestones</u>

1. Development of a fabrication process of chiral and nonlinear optical composites of DNA

In the approach made towards fabrication the DNA composites we capitalized on our experiencein preparation of samples of solutions of DNA in deionized water and DNA-cetyltrimethylammonium (DNA-CTMA) complex in butanol, processing of films, measurements of spectroscopic and optical properties of the samples.[1-7] We measured the refractive index of DNA and DNA-CTMA films with a prism coupler. We showed that

DNA films are birefringent and humidity-dependent but DNA-CTMA films are almost isotropic and weakly dependent on the relative humidity, RH.[2,4]
Refractive indices of DNA films n(TE) were about 1.54, n(TM) about 1.56 at RH 50% . They become smaller with an increasing humidity level. Refractive indices of DNA-CTMA films were about 1.51 at RH 50%. The n values changed and formed a hysteresis vs RH when a DNA-CTMA film was subjected to a humid environment.

2) Study of linear chiroptic properties, spectroscopic and microscopic properties of the hybrid nano-materials

DNA is a chiral template which has a relatively low chirality on its own; the specific rotation at visible wavelengths is 156 deg cm^2 g^{-1}. It increases more an order of magnitude at shorter wavelengths when the absorption band (λ_{max} 260nm) is approached.
However, DNA can be used to fabricate materials in which chromophores such as organic dyes or nanoparticles can be bound to the DNA helix and acquire a chiral structure thus contributing to the overall optical activity. The intercalation and electrostatic binding of a dye change the absorption spectra of DNA. These processes are conveniently monitored through circular dichroism (CD) measurements of the difference in absorption of left and right-handed circularly polarized light. We measured CD spectra in the 220 - 700 nm range in a number of systems in order to identify the DNA composites with enhanced chiral properties. The usual CD spectral signatures of the double helix were observed in DNA, and the derivative, DNACTMA complex in the 220-300 nm range. The CD bands were modified in the presence of a stilbene dye, triphenylamine and derivatives. Intercalating dyes such as ethidium bromide give remarkably stronger CD signals at longer wavelengths on binding to DNA, depending on the dye concentration, and thus provide indications of increased chiralities.

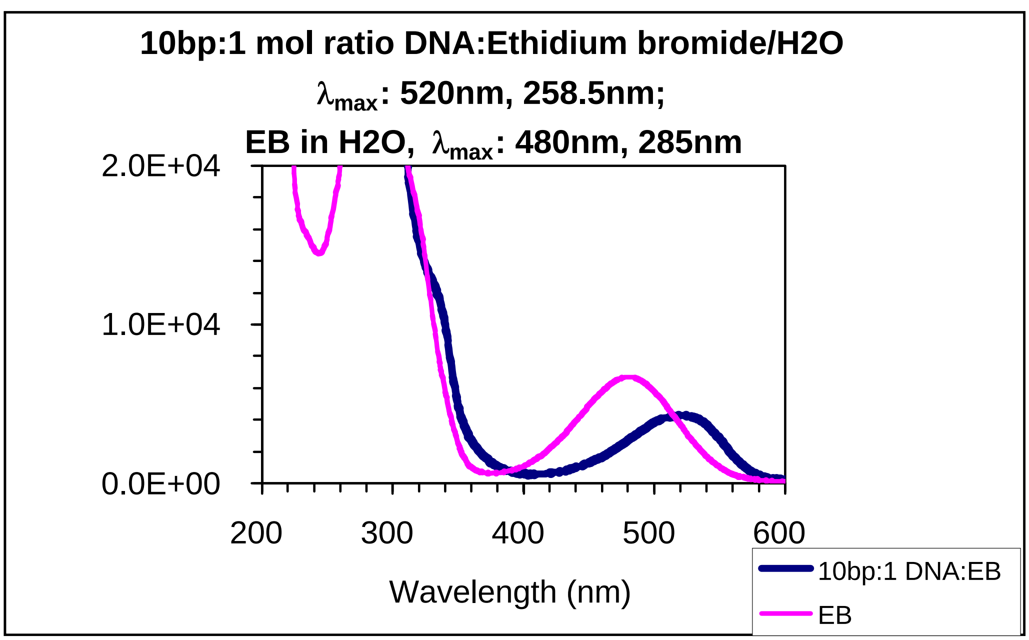

Fig. 1 shows an about 40 nm shift of the absorption maximum at 480nm to longer wavelengths in the spectrum of ethidium bromide in water upon binding to DNA.

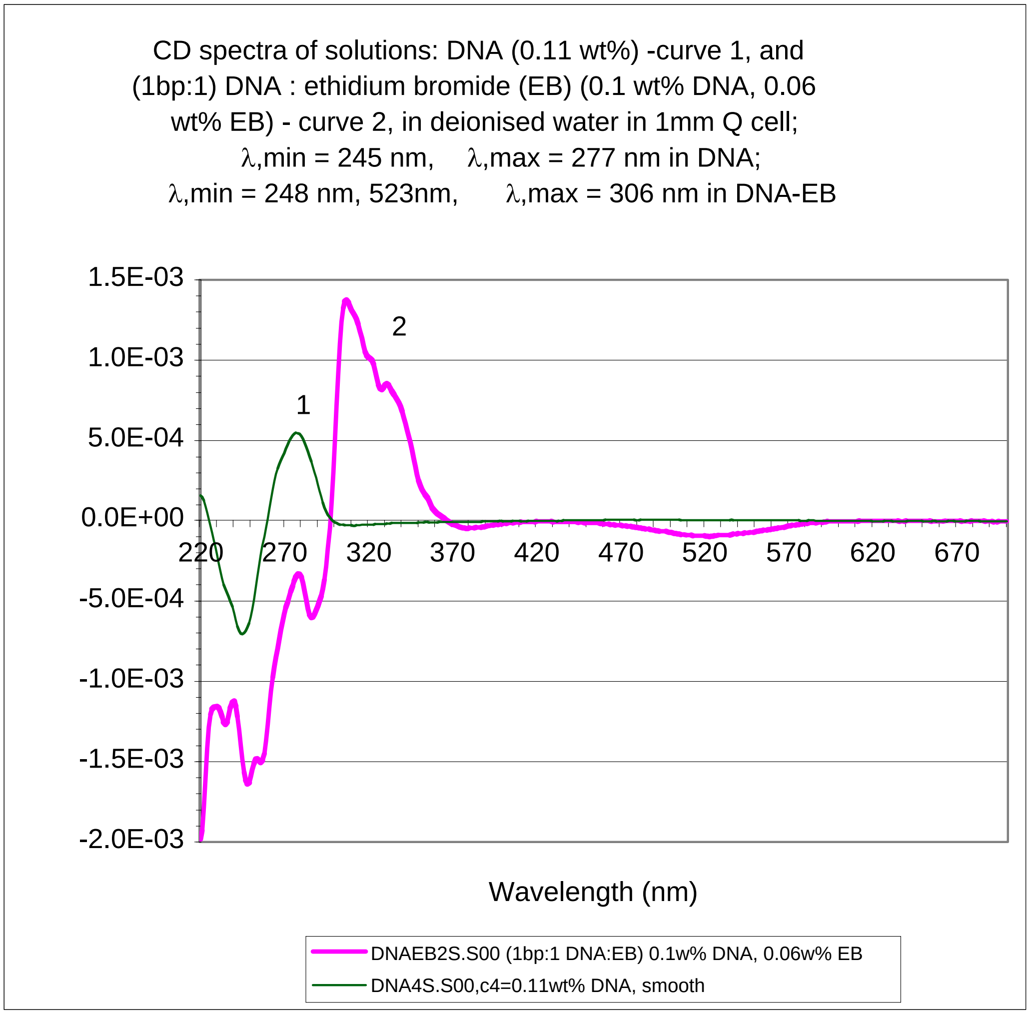

Fig 2 shows a new CD band appeared in the CD spectrum of DNA intercalated with ethidium bromide (the neat dopant does not show a CD band)

Several other dyes have been selected for mixing with DNA in water resulting in good optical films. But other dyes gave rather unsatisfactory results upon mixing with DNA-CTMA either in butanol or a mixture of butanol and chloroform; nonuniform, highly scattering layers were formed.

The dye-doped films were studied with a specular reflectance technique. The reflectance spectra of the composite DNA films were analyzed with the Kramers-Kronig transform to evaluate the dispersion of n and of the absorption coefficient k.

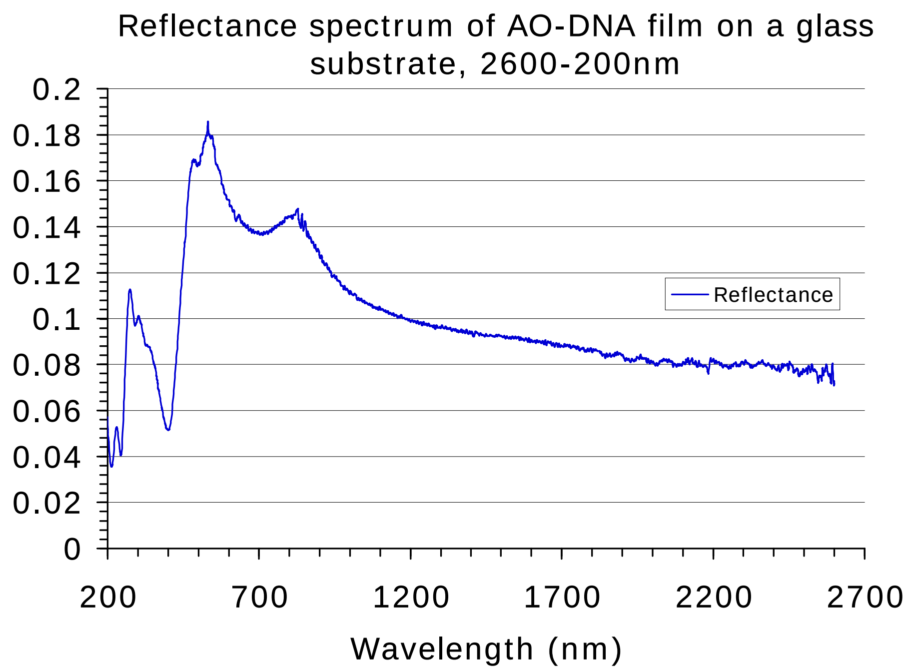

Fig. 3 shows reflectance spectrum in the film of DNA doped with Acridine Orange. R,max is at 530nm, R,min at 400nm. The additional reflectance maximum at about 850 is an artifact.

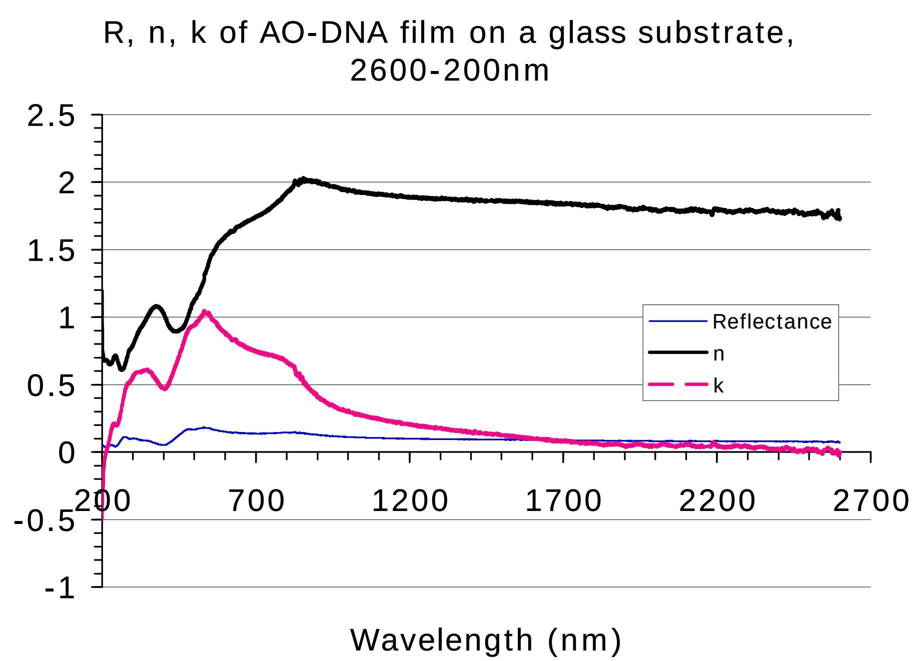

Fig. 4 shows anomalous dispersion and reduction of the refractive index to a value about 0.9 at about 440 nm.
R,max at 530nm, R,min at 400nm; k,max at 530nm, k,min at 400nm; n, max at 850nm (artifact!), n,min at 438nm

Other composite materials showed smaller reduction of n in the wavelength range close to absorption resonances but this may be due to lower quality of films.
The work on specular spectroreflectometry in the films which are highly specularly reflective, exhibit absorption and anomalous dispersion needs to be undertaken.

The microscopic properties of neat DNA and DNA-CTMA films have been previously studied.[5] They can form lyotropic liquid crystalline phases. Doping DNA with Stilbene 3 dye gave opaque polycrystalline layers.

3) Developing a sensitive apparatus to measure optical rotary dispersion (ORD) and circular dichroism (CD) in small volume samples and thin films

One of the important measurement capabilities needed to carry out the present project is the possibility of evaluation of chirooptic properties of samples which are prepared in the form of solid films. Such samples may exhibit considerable absorption of light at the wavelength of interest, due to the presence of chromophores and/or metal nanoparticles. In addition, the optical quality of some samples may also be not optimal. In view of these requirements we decided to adopt a reflectance modulation technique for the measurement of the chirooptic effects. Standard CD instruments are not suitable for such measurements.
The experimental setup for measurements of chirality by a sensitive retroreflection technique has been constructed. It is under testing.

4) Studies of nonlinear optical and chirooptical effects in DNA nano-composites with femtosecond Z-scan

The nonlinear optical (NLO) properties of DNA have been published.[1,3,6] Nonlinear refractive index of DNA is positive in a broad visible – near infrared range. Another opportunity in DNA composites lies in the fabrication of materials of very strong optical nonlinearity also through the binding of suitable nonlinear chromophores. This is being investigated by femtosecond NLO measurements of nonlinear refractive index n_2. We undertook effort to identify materials to be considered as potential NLO dopants, measure n_2 and the NLO dispersion.
The increase of both the chirality and the optical nonlinearity of DNA composites is of interest for fabrication of negative index materials because chirality can be used to provide a mechanism for achieving a negative index and nonlinearity may add to that by allowing either to switch the NIM into the territory of positive indexes or, opposite, provide a way to switch from a positive to negative index.

Future work
- Optimization of formation of high quality films of intercalated DNA
- Theoretical and experimental work on the DNA chiral composites with good film forming ability, which show strong, sharp resonances in the reflection spectra at visible frequencies

- Work on reflectance spectra of composite films to evaluate n and k dispersion.
- Evaluation of the possibility of obtaining negative refraction of a visible light beam in nano-composites of DNA with noble metal nanoparticles. Measure reflectance spectra of films of DNA composites in the presence of surface plasmon resonances induced by inclusions of gold nanoparticles.

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